PRELIMINARY STUDY ON THE RELATIONSHIP OF THE DDTS RESIDUES IN WILD SEA BASS AND SEAWATER

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Introduction

Dichlorodiphenyltrichloroethane (DDT) and its metabolites, dichlorodiphenyldichloroethane (DDD) and chlorodiphenyldichloroethylene (DDE) are persistent, lipophilic, and liable to bioaccumulation and biomagnifications (Guo et al. 2009). DDTs are designed as the sum of *o,p'*- and *p,p'*-DDT, DDD, and DDE. As a result of agricultural activities, DDT had been widely used for pest control and mosquito abatement prior to the global ban with a long history, and it has been suggested that the long history of widespread use of DDTs, may be responsible for substantial accumulation of DDTs (Fu et al., 2003; Zhang et al.,2007a). It has been also suggested that oceans act as a final sink for DDTs, and these compounds can be biomagnified in marine food webs and subsequently induce various toxic effects in humans after consumption (Binelli et al., 2003). With the gradual perfection of measurement technology of DDTs in organism, some organisms such as fish, seashell etc., had been used as biomarker for environmental monitoring and to evaluate the pollution situation in their living environment. Since wild sea bass is a kind of popular seafood for the residents living in coastal areas of Bohai sea and Yellow sea, which relatively easy to catch, it was chose as the objective for this study, while accompanied with the synchronous analysis on Chinese prawn as an auxiliary verification. In this study, DDTs in seawater, wild sea bass and wild Chinese prawn from Bohai sea and Yellow Sea were analyzed to research the relationship between the DDTs levels in organism and in seawater.

Materials and methods

Samples of sea bass, Chinese prawn and sea water were collected along the coast at 8 sampling sites in Bohai Sea and Yellow Sea area of China on April 2007. Details of the sampling locations were shown in Fig.1.

Fig.1 Sampling locations in Bohai Sea and Yellow Sea

The preparation/extraction of seabass and Chinese prawn samples followed the procedures described in detail previously (Shi et al. 2011). Briefly, the concentrated extract was passed through a NH2 solid phase extraction (SPE) cartridge (2g, 6mL, Supelco, USA). The concentrated eluate was then passed through a silica solid phase

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extraction (SPE) cartridge (2g, 6mL, Supelco, USA). A mixed solution of deuteratedphenanthrene, deuteratedpyrene, and deuterated chrysene was added to the eluate as an injection internal standard for injection to GC-MS.

Briefly, each Sea water sample (20L) was added ^{13}C-labeled *p,p'*-DDT, and filtered through Quartz Fiber Filter (QFF) and 18C filter (9mm, 3M) in turn. The QFF and 18C filter were extracted by Accelerated Solvent Extraction (ASE300, Dionex) and then cleaned up by Florisil column (1000mg, 6mL,SUPELCO) . Same injection internal standard as above was added into the concentrated eluate for injection to GC-MS.

The determination of Organnochlorine Pesticides (OCPs) was performed on a Shimadzu GCMS-QP2010 equipped with a fused silica capillary DB-5MS column (30 m × 0.25 mm i.d., film thickness: 0.25μm) using electron ionization with selective ion monitoring mode. High purity (99.99%) helium was used as carrier gas at 0.98 mL.min^{-1}. 2μ L of each sample was injected in spiltless mode.

Analysis was undertaken under strict QA/QC procedures, including analysis of procedural blanks, analytical reliability, recovery efficiency and accuracy. None of the target compounds were detected in the procedural blanks. Spiked samples were determined with nice precision recoveries of added pesticides (100ng OCPs) in samples ranged from 66.8% to 149%. Surrogate compounds were used to ensure the quality of the monitoring data, ^{13}C- labeled *p, p'*-DDT was added to all the samples before extraction, and the recoveries ranged from 71.5–130%. 10.0ng of OCPs mixture was added in 5.0g of Sea bass muscle and analyzed with every set of six samples. The standard deviation (SD) was calculated, 3SD were defined as method detection limit. The method detection limits were ranged from 0.04 to 0.18 g.kg^{-1} for OCPs.

Results and discussion

DDTs were the primary contaminants in all samples, with the concentration in seawater ranged from 0.151 to 6.57 g·L^{-1}, and in sea bass and Chinese prawn were 18.0-2,089 g·kg^{-1} wet wt and 0.764-28.7 g·kg^{-1} wet wt, respectively. Similar compositional patterns of OCPs in sea bass, Chinese prawn and sea water had been shown, with a ratio of 86.9 to 100% of the total OCPs. Thus the discussions in this study base on the data of DDTs level in sea bass, Chinese prawn and seawater. Compared with the data from other seaboard area in China, the DDTs concentrations of seawater in Bohai Sea (range 0.151-1.41 ug·L^{-1}) and Yellow Sea (range 0.339-6.57 ug·L^{-1}), were lower than those in Daya Bay (Aquacultural area, range 26.8-976 ug·L^{-1}, Zhou et al., 2001), higher than Pearl river (Baietang, range 0.03-0.55 ug.L^{-1}, Lou et al., 2004), and close to South China Sea (range 0.10-1.62 ug·L^{-1}, Zhang et al., 2007b) and Hongkong (Coastal, range 0.74-5.58 ug·L^{-1}, Wurl et al., 2006) respectively, which preliminary indicated that there were slight DTTs residue in Bohai Sea water and Yellow Sea, while in a relative better situation than some seaboard areas in China. Compared with the seawater wild fish (range 236 ng·g^{-1} lipid wet) in Pearl river (Guo et al., 2009), the DDTs concentrations of wild sea bass in Bohai Sea water (range 18.0-160 g·kg^{-1}wet wt) and Yellow Sea (range 33.3-2,089 g·kg^{-1}wet wt) showed a similar trend with seawater.

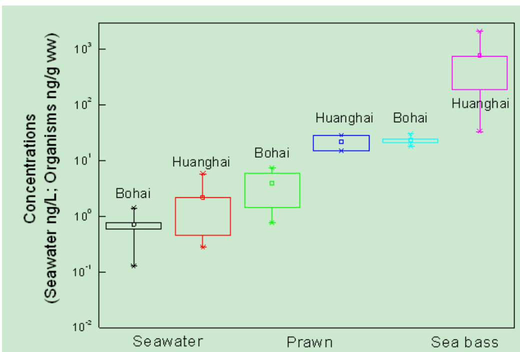

Fig.2 Comparison of DDTs levels in sea bass, Chinese prawn and seawater from Bohai Sea and Yellow Sea

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In general, the DDTs levels in sea bass from the Yellow Sea (range 33.3-2,089 g·kg^{-1}wet wt) were higher than those from Bohai Sea (range 18.0-160 g·kg^{-1}wet wt). A similar trend was also observed in the Chinese prawn samples, with DDTs concentrations of a range from 0.764 to 7.43 g·kg^{-1}wet wt in Bohai Sea and a range from 15.0 to 26.7 g·kg^{-1}wet wt in the Yellow Sea. This common trend might relate to their living environment. As shown in Fig.2, the concentrations of DDTs in seawater of Bohai Sea (range 0.151-1.41 ug·L^{-1}) were lower than that in Yellow Sea (range 0.339-6.57 ug·L^{-1}), it was preliminary demonstrated that aquatic organism, such as sea bass and Chinese prawn, could be used as biomarker which could characterize the contamination level of DDTs in seawater.

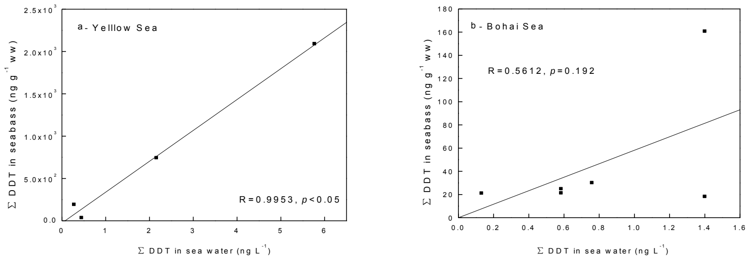

Fig.3 Relationship between the DDTs in seawater and in sea bass - Without normalization

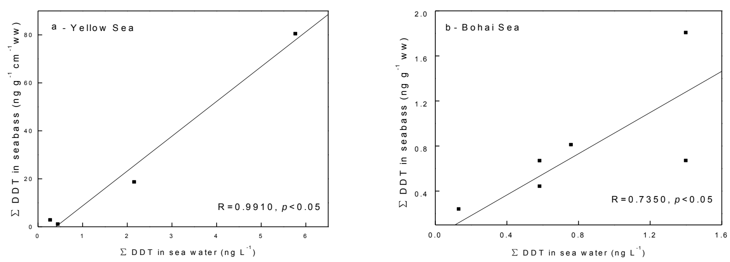

Fig.4 Relationship between the DDTs in seawater and in sea bass - After normalization

Further study was trying to find the relateionship between the DDTs in seawater and in sea bass. As shown in Fig.3a, a liner correlation (R=0.9953, $p<0.05$) between DDTs concentrations in sea bass and seawater well displayed that the concentrations of DDTs in organisms are significantly rising with those in their living environment. However, there was no relateionship found between DDTs in sea bass and seawater of Yellow Sea (R=0.5612, $p<0.192$). Previous studies had proved that the concentrations of DDTs in wildlifes would increase along with their growing period raise. Furthermore generally, the length of sea bass is correlated to their growing period. Thus a significant correlation of DDTs in seawater and sea bass from Yellow Sea was built when the fish body burden DDTs was nomalized by their length (Fig.4b, R=0.7350, $p<0.05$). The positive liner correlation was displayed after normalization by the growing period, which was not shown certainly just before normalization. It was indicated that when choosing sea bass or other perennial aqutic organisms as biomarker, growing period was an important factor. In other words, bioconcentration speed is accelerated as the raising of the sea bass's growing period, and the slope of DDTs in sea bass compared with those in sea water was 359 (Fig.3a), which was much larger than the slope of DDTs/length compared with DDTs in seawater (13.2, Fig.4a).

Aquatic organisms such as sea bass and prawn are ideal biomarker of seawater pollution. On one hand, the contaminants concentrations in wildlife could estimate the pollution condition in their living environment. On the other hand, it could also estimate the pollution trend and exposure risk of organisms given the consideration of other factors like growing period ect. Due to only a few number of samples analyzed in this study, additional research is required to further evaluate the correlation between the characters of the sea bass, as a biomarker, and the DDTs level in seawater of Bohai sea and Yellow sea.

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